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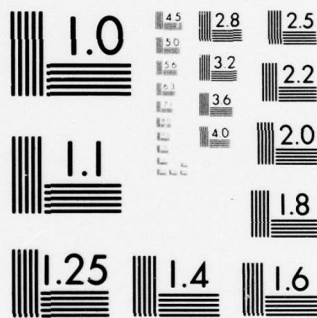
ARMY MATERIALS AND MECHANICS RESEARCH CENTER WATERTO--ETC F/6 11/5
THE POTENTIAL FOR ACCIDENTAL RELEASE OF CARBON/GRAPHITE FIBERS --ETC(U)
JAN 79 S E WENTWORTH, A O KING, R J SHUFORD
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**THE POTENTIAL FOR ACCIDENTAL
RELEASE OF CARBON/GRAPHITE FIBERS
FROM RESIN MATRIX COMPOSITES
AS DETERMINED BY THERMO-
GRAVIMETRIC ANALYSIS**

January 1979

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ABSTRACT

Recently, there has been concern over the effects of accidentally released conductive carbon and graphite fibers on unprotected electrical circuits. Since involvement in fire would be the principal means of release of these fibers from resin matrix composites, the thermal oxidative behavior of such materials became a matter of interest. Thus, a series of dynamic and isothermal thermogravimetric analyses was performed on a variety of state-of-the-art materials. The dynamic analyses (10 C/min, flowing air) indicated the temperatures at which the resin matrices and fibers experienced the onset of degradation. Isothermal analyses at 400 C and 500 C in flowing air were used to determine the time at temperature required to generate releasable fibers. Microscopy was used to examine the residues in order to characterize their physical state. It was concluded that the potential for accidental release varied inversely with the thermal stability of the resin matrix and directly with that of the fiber.

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INTRODUCTION

The ever-growing emphasis on fuel-efficient aircraft and vehicles has led to a rapidly expanding utilization of carbon and graphite fiber resin matrix composites. While presently confined largely to aircraft (primarily for economic reasons), it is projected by the mid 80's the average passenger car will contain 400 to 500 pounds of such materials. The wide-spread distribution of such large amounts of these materials has led to concern relative to the accidental dispersion of carbon and graphite fibers.^{1,2} Because of the highly conductive nature of these fibers, contact with unprotected electrical and electronic circuits can cause a variety of problems including resistive loading, temporary short circuits, and arcing. Any of these can lead to immediate equipment failure.

Since the principal means of release of these fibers from resin matrix composites would be involvement in a fire, the thermal and thermal oxidative behavior of these materials became of interest. Accordingly, a number of state-of-the-art aerospace materials as fabricated and supplied by several of the major airframe manufacturers were subjected to dynamic and isothermal thermogravimetric analysis in order to assess their potential for fiber release under thermal oxidative stress. The materials so examined are indicated in Table 1.

It is strongly emphasized that the designation of materials fabricators and identification of resins and fibers by commercial designation is solely for the purpose of adequate materials description. Conclusions regarding these materials relate only to intrinsic materials properties and are not to be construed as impugning the quality of any given material. Such conclusions address only the potential for release and dispersal of conductive fibers.

Table 1. MATERIALS STUDIED

SUPPLIER	MATERIAL FIBER/RESIN	FIBER TYPE PRECURSOR/MODULUS	RESIN TYPE
GENERAL DYNAMICS	CELION 6000/5208 T6300/5208 T300/5208 T300/934 AS/3501 T300/F178	PAN/INTERMEDIATE	EPOXY
LOCKHEED/SUNNYVALE	UC PITCH/934 T300/5208 T300/F178 T300/PMR-15 AS/2080	PITCH/UNKNOWN PAN/INTERMEDIATE	POLYIMIDE EPOXY POLYIMIDE
LOCKHEED/GEORGIA	T300/5208 AS/3501 UMA/976 GY70/7534	—/— PAN/HIGH	EPOXY
LOCKHEED/BURBANK	T300/5208 T300/934	PAN/INTERMEDIATE	
MCDONNELL/DOUGLAS	T300/5208 AS/3501		
NORTHROP	AS/3501		
GRUMMAN	AS/3501		
MIT	MOD III/PPQ		POLYQUINOXALINE
NASA/LOCKHEED	HTS/PMR-15		POLYIMIDE

1. *A Report of Observed Effects on Electrical Systems of Airborne Carbon/Graphite Fibers.* NASA Technical Memorandum 78652.
2. *Carbon Fiber Study.* Intergovernmental Committee, NASA Technical Memorandum 78718, May 1978.

EXPERIMENTAL

Sample Preparation

Materials for these tests were received from the fabricators in a variety of shapes and sizes, i.e., thin and thick plates, tension specimens, etc. They were stored under ambient conditions until testing. The samples for thermal analysis were obtained by cutting roughly rectangular pieces weighing generally 3 to 8 mg from the larger specimens with a jeweler's saw.

Thermal Analysis

All thermal analyses were performed with an unmodified Perkin Elmer TGS-2 Thermogravimetric System. An atmosphere of flowing air (50 ml/min) as delivered from a cylinder of dry air was used throughout. Dynamic analyses were conducted at a heating rate of 10 C per minute. Isothermal analyses were performed by bringing the samples from ambient to 400 C or 500 C as appropriate at a rate of 40 C per minute. Raw data in the form of strip chart recordings were digitized and stored on magnetic tape by means of a Hewlett-Packard 9830B calculator equipped with a 9864A digitizer. The associated 9862A calculator/plotter was subsequently used for plotting and cross plotting of the stored curves.

Macrophotography and Microscopy

Low magnification macrophotographs were obtained with a Polaroid Land MP-3 Multipurpose Industrial View camera. Scanning electron microscopy was performed with an AMR-900 scanning electron microscope.

RESULTS AND DISCUSSION

It is to be emphasized at the outset that the thermogravimetric analyses to be discussed are in no way intended to represent a realistic model of a fire involving the materials under consideration. A fire is a complex environment which results from the interaction of a number of factors including heat and oxygen. It is these factors which thermogravimetric analysis addresses. By running a series of materials under the same conditions, it is possible to rank them as to relative thermal oxidative stability. In the present study, the objective was twofold: to determine temperatures at which significant events take place, and to determine the effect of time at a given temperature on the physical state and longevity of residual material. These determinations require two distinctly different experiments. The former are obtained from dynamic analyses while the latter from isothermal aging.

Dynamic Analyses

The dynamic analyses were all run at a constant heating rate of 10 C per minute in flowing air, weight loss being recorded as a function of temperature. A typical curve is shown in Figure 1. Several important features indicated by arrows are illustrated here. Initial weight loss indicates the temperature at which weight loss is first detected. Resin decomposition indicates the temperature corresponding to the first major break in the weight loss curve. Fiber decomposition

corresponds to the temperature at which the fibers begin to experience oxidative degradation. The intermediate break, which is not labelled, is the temperature at which the char formed by the resin decomposition begins to undergo oxidative degradation. Such char formation is not observed with all the resins examined but appears to be characteristic of the epoxies. The identity of these points was established by comparison with the thermogravimetric analysis curve for a neat cured 5208 resin as shown in Figure 2. As can be seen, the neat resin shows two break points corresponding in temperature to the first two break points for the typical graphite fiber composite based on the same resin. The third break point is completely absent from the neat resin and is thus ascribed to the fiber. Table 2 lists the characteristic temperatures for the materials studied.

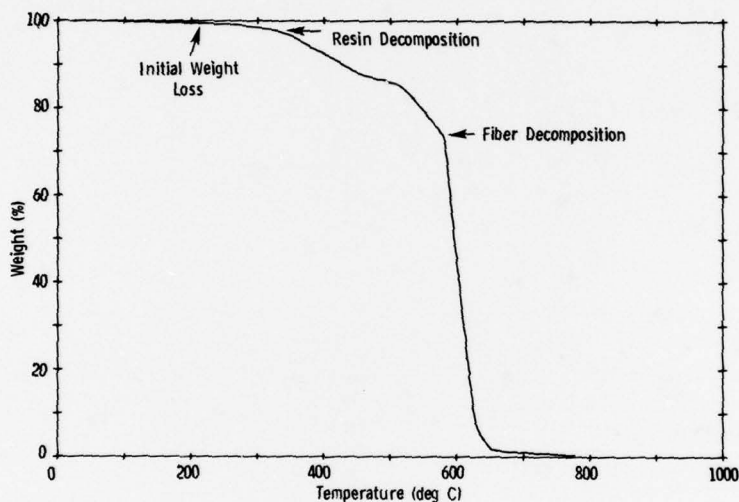


Figure 1. Typical dynamic thermogravimetric analysis — AS/3501 combination.

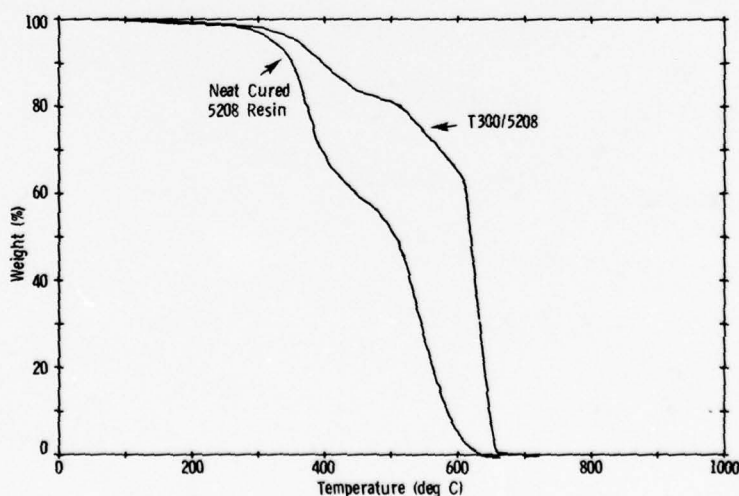


Figure 2. Comparison of dynamic thermogravimetric analyses of neat cured 5208 resin and T300/5208 combination.

Several generalizations are possible. Firstly, initial weight loss temperature is not a significant parameter in terms of potential for fiber release. It varies from ambient for an epoxy (934) to 520 C for the polyquinoxaline. In most cases, it does not reflect resin decomposition but rather loss of adsorbed moisture and/or solvent. Secondly, the same material from different suppliers shows, as would be expected, rather similar behavior. For example, Figure 3 shows the T300/5208 combination from five different sources. As can be seen, the pattern is the same for all five. Indeed, four are nearly superimposable. The Lockheed/Sunnyvale material lies below the others because of a higher resin content. Even so, the characteristic temperatures for this material fall in the same range as those of

Table 2. SIGNIFICANT TEMPERATURES AS DETERMINED BY DYNAMIC TGA

SUPPLIER	MATERIAL FIBER/RESIN	TEMPERATURE IN DEGREES CELSIUS FOR		
		INITIAL WEIGHT LOSS	RESIN DECOMPOSITION	FIBER DECOMPOSITION
GENERAL DYNAMICS	CELION 6000/5208	270	345	720
	T6300/5208	165	345	645
	T300/5208	210	360	642
	T300/934	175	345	635
	AS/3501	-	324	591
	T300/F178	115	386	619
LOCKHEED/SUNNYVALE	UC PITCH/934	AMBIENT	292	770
	T300/5208	110	364	610
	T300/F178	140	387	617
	T300/PMR-15	-	559	559
	AS/2080	100	603	603
LOCKHEED/GEORGIA	T300/5208	270	343	632
	AS/3501	185	342	602
	UMA/976	80	310	715
	GY70/7534	175	327	876
LOCKHEED/BURBANK	T300/5208	130	347	621
	T300/934	135	342	635
MCDONNELL/DOUGLAS	T300/5208	135	358	602
	AS/3501	200	354	593
NORTHROP	AS/3501	-	340	592
GRUMMAN	AS/3501	190	345	600
MIT	MOD II/PPQ	520	623	687
NASA/LOCKHEED	HTS/PMR-15	370	571	800

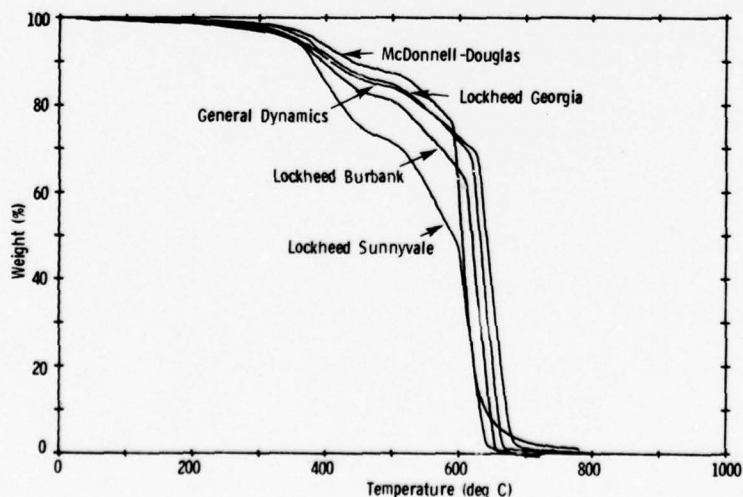


Figure 3. Comparison of dynamic thermogravimetric analyses of T300/5208 combination from different suppliers.

the other four. Thirdly, different resins from the same category exhibit similar behavior. Figure 4 compares three different polyimides. None shows significant weight loss below 400 C and all produce decomposition products which apparently undergo thermal oxidative degradation at rates comparable to those of the fibers. Figure 5 compares three nominally different epoxies. Here the similarity is striking, especially for the resin-controlled portion of the curves. Thus, it is not surprising to learn that the three resins are actually chemically identical, consisting of N,N,N',N',-tetraglycidylmethylenedianiline (TGMDA) cured with 4,4'-diaminodiphenylsulfone (DDS).

As to the relevance of these experiments to potential release of conductive fibers, the following comments can be made. With regard to the influence of resin type, Figure 6 clearly shows that the extremely stable PPQ survives, and therefore is available to bind fibers, to a significantly higher temperature than either the epoxy (5208) or the polyimide (PMR-15). Insofar as fiber type is concerned, the opposite effect obtains. That is, the more stable fiber has greater potential for dispersal simply because it survives to higher temperatures. Figure 7 demonstrates

Figure 4. Comparison of dynamic thermogravimetric analyses of various polyimide-based combinations.

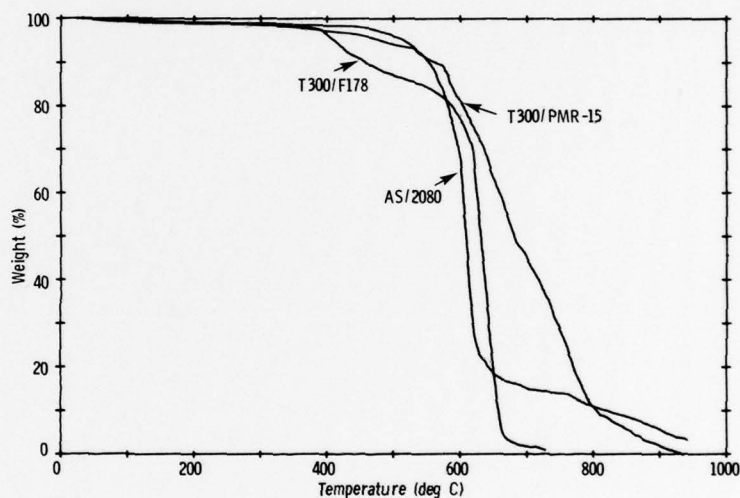
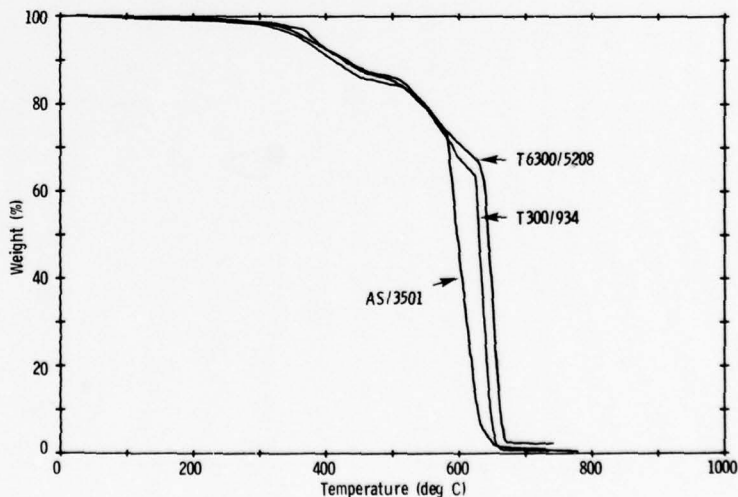


Figure 5. Comparison of dynamic thermogravimetric analyses of combinations based on nominally different epoxies.



this effect most graphically. The AS/3501 is a thermaloxidatively labile fiber in an epoxy resin whereas the GY70/7534 is an extremely stable fiber in another epoxy resin. The resin-controlled portions of the curves are rather similar in contrast to the fiber-controlled portions which differ radically. The AS fiber survives only a short time after the resin char has been consumed. The GY70, on the other hand, persists to very high temperatures. In fact, at 920 C at least two thirds of the fiber remains. Thus, the lack of stability of the AS fiber is an asset in terms of potential for accidental release as a result of fire. Obviously, a much hotter fire is required to totally consume the GY70 fiber.

The dynamic analyses have been very useful in indicating temperatures at which resin matrices decompose and at which dispersible fibers are generated. Because of the nature of the experiment (fixed rate of temperature increase) the technique does not address the effect of time at temperature. Stated another way, it does not provide information relative to the question "How long does it take for a given set of conditions to produce releasable fiber?" For this, isothermal aging is the method of choice.

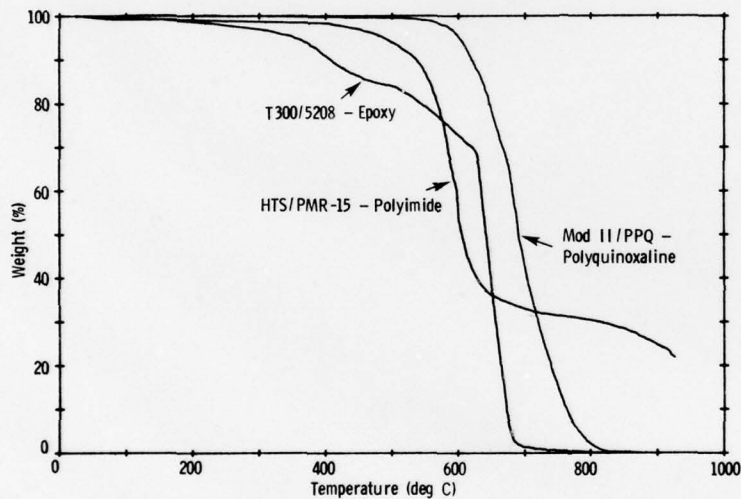


Figure 6. Influence of resin type on dynamic thermogravimetric behavior.

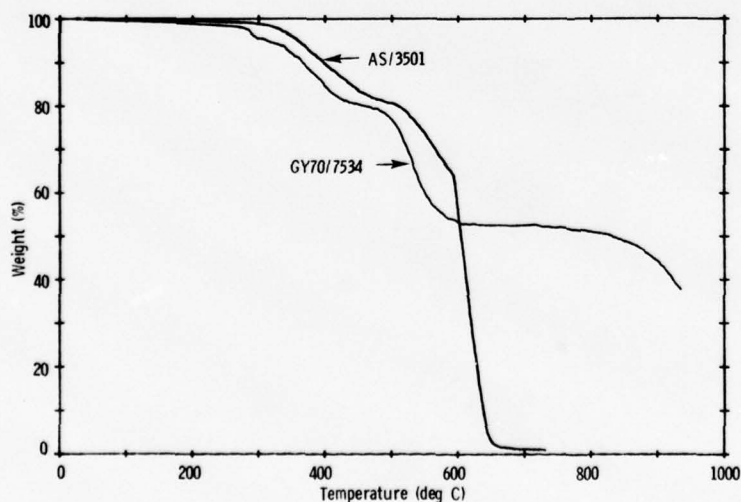


Figure 7. Influence of fiber type on dynamic thermogravimetric behavior.

Isothermal Aging

The isothermal aging experiments were all conducted in flowing air, weight being recorded as a function of time while temperature is held constant. Figure 8 shows a typical set of results for an epoxy-based material at the two temperatures selected for this study. These temperatures were somewhat arbitrarily chosen and reflect experimental convenience more than actual fire conditions. Lower temperatures would have required inordinately long times while higher temperatures would have resulted in such compression of data that discrimination between materials would have been lost. This figure illustrates the dramatic difference between the persistence of the material at 400 C and at 500 C. In both cases, there is a very rapid initial weight loss (actually occurring while the sample is being brought to temperature) which corresponds to resin decomposition to char. At 400 C the oxidative degradation temperature for the char has not been reached and, thus, it persists for several hours. At 500 C, however, the char undergoes rapid oxidation as do the residual fibers. These events are deduced by examination of Figure 9 in

Figure 8. Typical isothermal aging curves, 400 C and 500 C - AS/3501 combination.

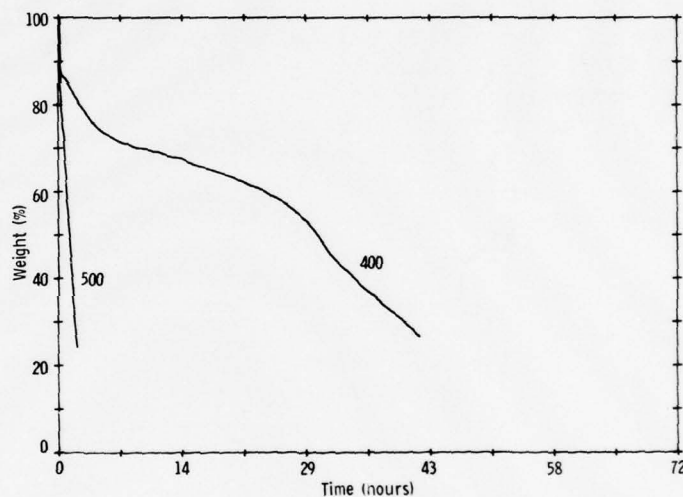
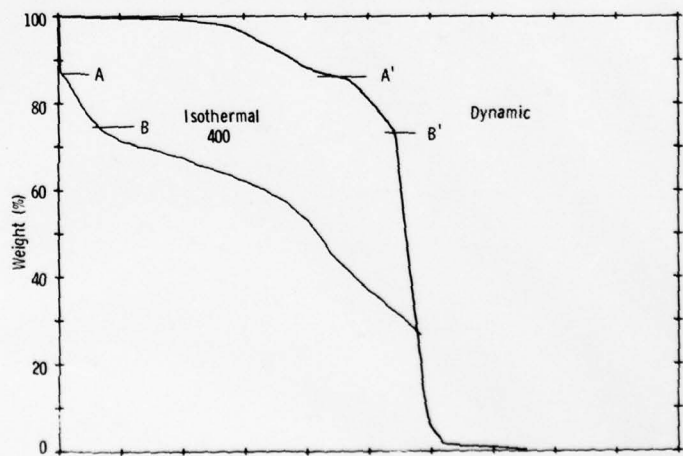


Figure 9. Comparison of dynamic and 400 C isothermal aging curves for AS/3501 combination.



which the dynamic analysis curve is superimposed on the 400 C isothermal run for this material. (Only the vertical weight percent coordinate is correct for the dynamic run.) As can be seen, there is good correspondence between the weight percent at the breakpoints A and A' and B and B'.

Isothermal aging results are most conveniently reported in terms of time required to reach a given weight loss such as half life (t_{50}). The results for the materials studied are reported in Table 3. The times to 20% and 50% weight loss were chosen for comparison in that the former reflects the contribution of the resin while the latter involves, at least to some degree, the fiber. While no prior data was available, it was presumed that the materials studied were 60 to 70 weight percent fiber. It is likely that a good deal of the variation in the results for similar materials (e.g., T300/5208 and T300/934, Figure 10) is due to variation in resin content. Thus, if a material is 50% resin it can obviously degrade to 50% weight much faster than a material which is only 20% resin. In spite of this variation several generalizations are possible.

As suggested above, higher aging temperatures cause a compression in data such that differentiation between materials is difficult. This is clearly evident in the 500 C results, especially for the t_{20} values which reflect resin contribution. Only the extremely stable polyquinoxaline has a t_{20} greater than two hours. The polyimides, as a class, show only slightly better performance than the epoxies, ranging from 0.5 to 1.5 hr as compared to 0.2 to 0.4 hr for the epoxies. The t_{50} values which are partially fiber-controlled are more discriminating. In two cases, UC Pitch/934 and GY70/7534, the fibers are extremely stable and persist long after

Table 3. FRACTIONAL LIVES AS DETERMINED BY ISOTHERMAL AGING

SUPPLIER	MATERIAL FIBER/RESIN	AGING TEMPERATURE, DEGREES CELSIUS			
		400		500	
		t_{20} hr	t_{50} hr	t_{20} hr	t_{50} hr
GENERAL DYNAMICS	Celion 6000/5208	3.5	*	0.3	12.5
	T6300/5208	2.3	35.0	0.2	3.6
	T300/5208	4.0	44.0	0.4	3.7
	T300/5208	3.7	35.7	0.3	3.5
	AS/3501	2.6	30.5	0.3	1.3
	T300/F178	10.0	42.5	0.5	2.0
LOCKHEED/SUNNYVALE	UC PITCH/934	1.8	†	0.3	†
	T300/5208	2.6	25.5	0.3	0.9
	T300/F178	6.0	†	0.5	2.7
	T300/PMR-15	9.5	38.0	1.5	4.7
	AS/2080	6.7	18.5	0.7	1.2
LOCKHEED/GEORGIA	T300/5208	3.2	46.0	0.3	2.7
	AS/3501	1.5	38.5	0.2	1.2
	UMA/976	1.3	*	0.2	25.0
	GY70/7534	3.0	*	0.3	*
LOCKHEED/BURBANK	T300/5208	1.7	36.0	0.2	2.2
	T300/934	1.3	23.0	0.2	2.7
McDONNELL/DOUGLAS	T300/5208	5.0	38.5	0.4	1.2
	AS/3501	0.3	7.2	0.3	1.2
NORTHROP	AS/3501	2.5	23.5	0.2	1.2
GRUMMAN	AS/3501	3.7	43.5	0.3	1.5
MIT	MOD II/PPQ	50.0	*	2.4	12.5
NASA/LOCKHEED	HTS/PMR-15	10.5	39.0	0.6	1.2

* > 50% AFTER 72 HOURS

† TERMINATED - HAD PLATEAUED > 50%

‡ TERMINATED < 50% FOR CONVENIENCE

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the resin has completely burned off. A few other fibers of intermediate stability show t_{50} 's in the 12- to 25-hour range. The bulk of the materials studied reached t_{50} in less than 5 hours. Figure 11 illustrates these three types of behavior.

The 400 C results provide a much better ranking in terms of thermal oxidative stability. The t_{20} values firmly establish the relative stabilities of the resins suggested by the 500 C results. The t_{20} values of the epoxies are all 5 hours or less while those of the polyimides all fall in the 6- to 10-hour range. The clear superiority of the polyquinoxaline is overwhelmingly demonstrated with a t_{20} of 50 hours. The t_{50} results mirror the 500 C results with the more stable fibers now surviving past the 72-hour period of the experiment. Figure 12 shows typical curves illustrating these types of behavior.

With regard to the bearing of these studies on the potential for release of fibers, a "best case" and a "worst case" can now be defined. The best case is clearly that of the Mod II/polyquinoxaline combination. Here the resin survives

Figure 10. Effect of resin content on 400 C isothermal aging behavior.

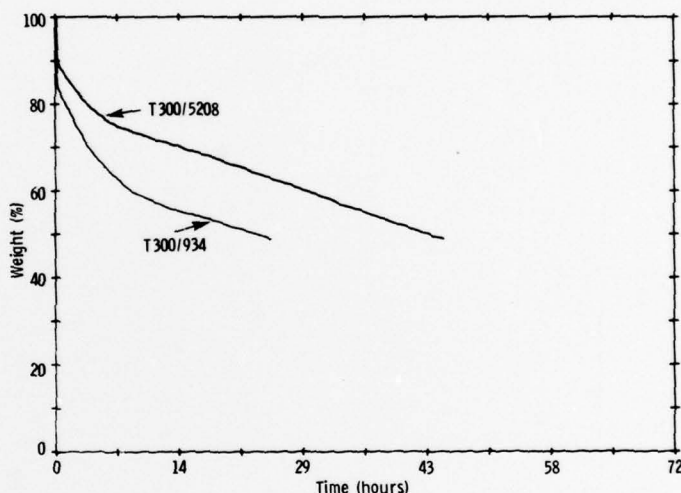
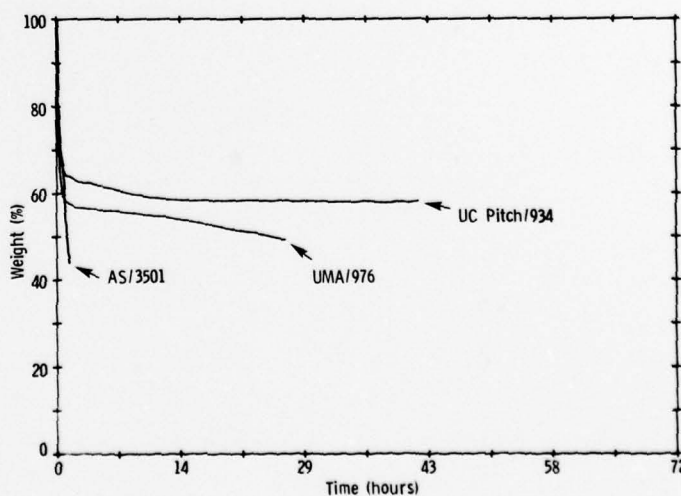


Figure 11. 500 C isothermal aging curves for combinations based on different fiber types.



for much longer periods at any given temperature than any of the other systems. Thus, it is available to bind the fibers long after other systems have degraded to free fibers. Conversely, the worst case is the GY70/7534 system. In this case, the resin is rapidly consumed to leave behind the extremely stable fiber in the free state. These extreme cases are shown in Figure 13. In fact, as Figure 14 shows, the situation is even worse at 500 C. Here the resin is very rapidly consumed and yet the fiber is still perfectly stable. This is not to single out the 7534 resin. In fact, any epoxy would yield the same results with this fiber.

Any other combination examined gives rise to an intermediate potential for release. Interestingly enough, two of the more favorable cases involve rather different types of materials. They are T300/F178 and AS/3501, shown in Figure 15. In the T300/F178, the moderately good stability of the polyimide resin is beneficial. In the AS/3501, the AS fiber has poor thermal stability relative to other fibers. Thus, it is more readily consumed after the resin has burned off thereby reducing its chances for dispersal.

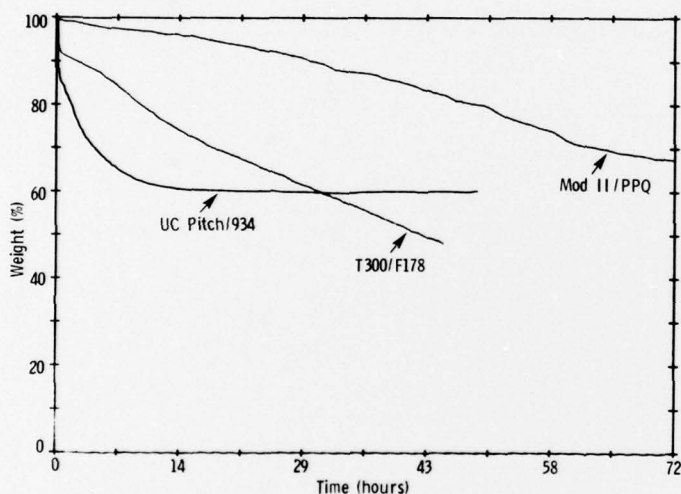


Figure 12. 400 C isothermal aging curves for combinations based on different resin types.

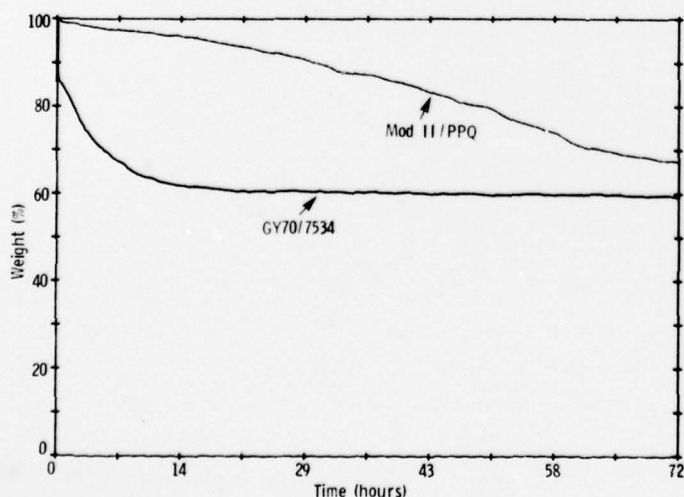


Figure 13. 400 C isothermal aging curves for "Best Case" (Mod II/PPQ) and "Worst Case" (GY70/7534).

Figure 14. Comparison of 400 C and 500 C isothermal aging curves for GY70/7534 (Worst Case) combination.

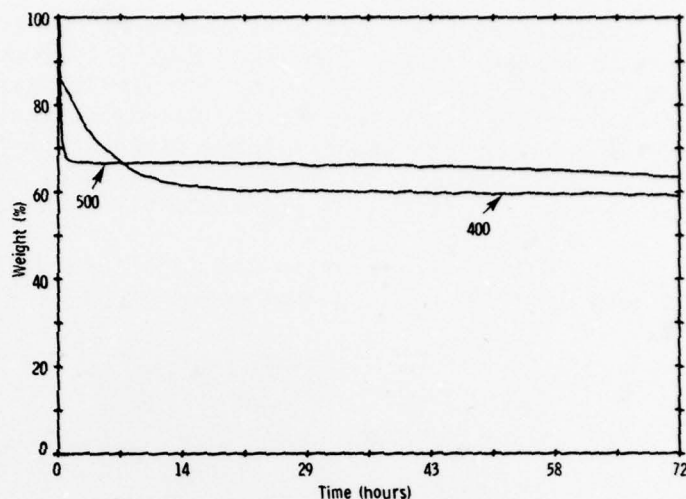
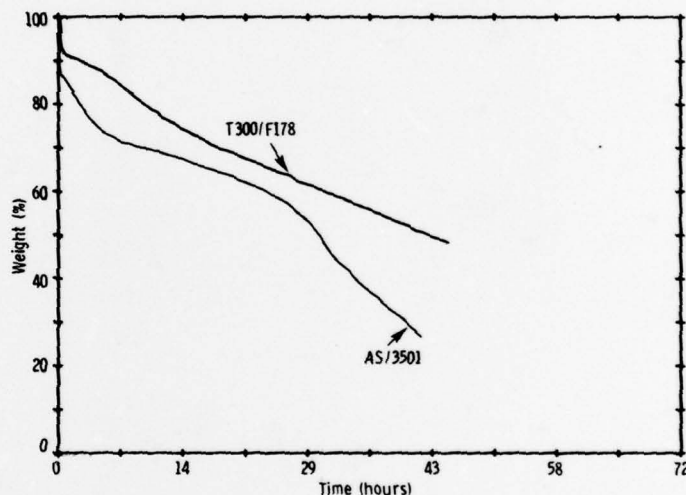


Figure 15. 400 C isothermal aging curves for T300/F178 and AS/3501 combinations.



Microscopy

In order to further assess the potential for accidental release, it was of interest to examine residual fibers by means of microscopy. Accordingly, photomicrographs and scanning electron micrographs were made of selected residues from both dynamic and isothermal thermogravimetric analyses. These studies provide support for the conclusions drawn from the thermogravimetric analyses as to the superiority of the thermally resistant resins for mitigating accidental release.

Figure 16 is a photomicrograph of the residue from the dynamic analysis of the GY70/7534 system (see Figure 7). Although this experiment was terminated at 920 C, nearly the upper limit of the instrument, a substantial residue remained. As can be seen, it consists entirely of loose individual fibers. Obviously, this sort of residue is free of binding resin and could be readily dispersed. Thus, the "worst case" designation for this system is supported by physical examination of thermogravimetric analysis residue.

Evidence of the beneficial nature of the thermally resistant resins is provided in the next three figures. Figure 17 compares photomacrographs of the residues from 400 C isothermal aging for similar periods of time of the T300/934 and AS/2080 systems. The less stable 934 epoxy resin has been completely consumed, leaving behind predominantly loose dispersible fibers. By contrast, the more stable 2080 polyimide has apparently formed a char which serves to bind the residual fibers into clumps of significantly reduced dispersibility.

Figure 18 shows high and low magnification scanning electron micrographs of residues from 400 C isothermal aging of the T300/5208 and T300/PMR-15 systems.

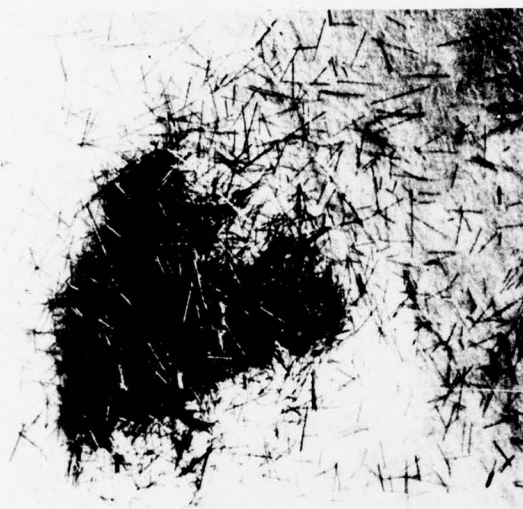


Figure 16. Photomacrograph of residue from dynamic thermogravimetric analysis of GY70/7534 (see Figure 7). Mag. 7X.



a. T300/934 (Epoxy)



b. AS/2080 (Polyimide)

Figure 17. Photomacrographs of residues of epoxy- and polyimide-based combinations after 400 C isothermal aging for approximately one day. Mag. 7X.



a. Mag. 17X

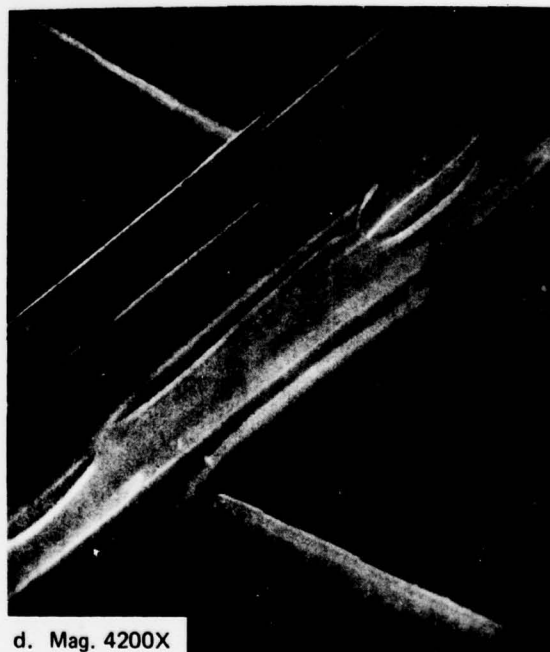


b. Mag. 4500X

T300/5208 (Epoxy)



c. Mag. 42X



d. Mag. 4200X

T300/PMR-15 (Polyimide)

Figure 18. Comparison of low and high magnification scanning electron micrographs of 400 C isothermal aging residues from epoxy- and polyimide-based combinations.

The superiority of the PMR-15 polyimide over the 5208 epoxy is clearly evident from the low magnification shots. Even though the PMR-15 based material was exposed for an additional 19 hours, almost no dispersible fibers are evident, in sharp contrast to the 5208 base material. Evidently the PMR-15 forms a stable char under these conditions. The high magnification shots of individual fibers are most interesting. That from the 5208 resin is completely clean while that from the PMR-15 appears to be coated with a sheath of what we believe to be resin char. This is beneficial from two points of view: (1) the char may serve to act as an insulator thereby mitigating the effect of contact with electrical circuits, and (2) the char certainly increases the weight of the fiber, thus reducing its potential for dispersal.

Finally, Figure 19 compares scanning electron micrographs of residues from 400 C isothermal aging of the T300/5208 and Mod II/PPQ systems. Here the superiority of the highly stable polyquinoxaline resin is most striking. Whereas the 5208 based material had produced loose fiber, the polyquinoxaline based material is still one homolithic chunk with no loose fibers evident. Thus, microscopic examination of residues provides strong support for the contention that thermally resistant resins are useful in reducing the potential for accidental release of fibers from advanced composites exposed to a thermal oxidative environment.



Mag. 17X

a. T300/5208 (Epoxy)



Mag. 40X

b. Mod II/PPQ (Polyquinoxaline)

Figure 19. Comparison of scanning electron micrographs of 400 C isothermal aging residues from epoxy- and polyquinoxaline-based combinations.

CONCLUSIONS AND RECOMMENDATIONS

It is very clear from the body of evidence presented above that the use of a high-temperature-resistant resin matrix significantly reduces the potential for conductive fiber release from advanced composites when they are subjected to a thermal oxidative environment. It is equally clear that high modulus fibers like GY70, because of their thermal oxidative stability, offer the greatest potential for release. This so-called "worst case" is aggravated by the fact that the property which controls thermal oxidative stability, degree of graphitization, also controls conductivity. Thus, the most stable fibers are the most conductive and the "worst case" designation is reinforced.

Based on these conclusions, it is strongly recommended that whenever high modulus fibers are used, a high-temperature-resistant resin matrix be considered as well. Further work in this area must include a validation of these thermogravimetric analysis based results with actual fire testing and an extension of the thermogravimetric analysis evaluation to carbon and graphite fiber-filled thermoplastics. These are the materials to be utilized in great volume by the automotive industry and thus constitute a far greater potential threat of accidental release.

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